Book Review

Relativistic Effects in Chemistry Part A: Theory and Techniques. *By Krishnan Balasubramanian, John Wiley & Sons, New York, 1997, 301pp. $84.95 (HB). ISBN 0-471-30400-X.*

There has been a great deal of interest lately in the inclusion of relativistic effects in quantum chemical calculations, stemming from the realization that these may not only affect the quantitative prediction of chemical properties but even alter the qualitative description. With more powerful computers it is now possible to incorporate relativistic effects into high-level calculations. The appearance of a book on relativistic effects in chemistry is therefore very timely.

The preface gives two discernible goals for the two volumes of the book. The first is to provide answers to questions concerning relativistic effects in chemistry. The second is to compile current techniques for relativistic quantum chemical computations and results accumulated to the present. The intention to present relativity in a chemical context is also implied in comments on quantum mechanics texts. The first volume, the subject of this review, is divided into five chapters: an introduction; a chapter on special relativity; a chapter on relativistic quantum mechanics; a chapter on relativistic quantum chemistry; and a chapter on double group symmetry.

In the introduction the author gives an overview of the importance of relativity in chemistry. The principal effects are treated at a basic, descriptive level of understanding illustrated with numerous examples. The presentation is marred by some oversimplifications and overstatements, a number of errors, the presence of material in tables that is not discussed in the text, and some irrelevant material. The chapter commences well, but becomes bogged down in a sequence of examples with no connecting thread between them, and simply ends in the details of an example, without ever surfacing to the general picture. Regardless of the somewhat meandering presentation, the importance of relativity in chemistry is certainly established.

The chapter on special relativity is treated on the assumption, stated in the preface, that the reader has had no exposure to the topic, and covers all the aspects of an undergraduate special relativity text and in much the same fashion. As an introduction to these topics, one would be better served by standard physics texts, which are more clearly presented, have many fewer errors, are more consistent in their notation and the level at which derivations are presented, and much better in their explanations of phenomena. For a book whose primary goal is the presentation of relativistic effects in chemistry this chapter has a lot of material that is irrelevant, and does not present at all well the relevant sections, such as the sections on electromagnetism and on angular momentum. In its favor it does make connections to chemistry from time to time, but does not really have the chemistry in view as a goal towards which the chapter is directed.

In a similar vein to the second, the third chapter contains the kind of material expected in a standard physics text introducing relativistic quantum mechanics, covering such topics as the Klein–Gordon and Dirac equations, solutions of the Dirac equation, the Foldy–Wouthuysen transformation, and the Breit–Pauli approximation. Like its predecessor, it is inferior to the standard physics texts. Inconsistent notation and missing definitions create confusion, along with the inaccuracies and errors that are sprinkled throughout the chapter. The same unevenness in the level of explanation as in the second chapter is evident. Some sections, such as that on relativistic angular momentum, are fairly well explained, but others such as the Foldy–Wouthuysen transformation, are not. The choice of the relativistic unit system in which $c = 1$ seems antithetical to the goal of a presentation to chemists who almost invariably use Hartree atomic units.

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The fourth chapter is extremely brief. After a very short description of the Dirac Hamiltonian for an atom and the Breit–Pauli Hamiltonian, the theory of effective core potentials (ECPs) is presented, followed by a summary description of configuration interaction methods and a small three-page section on semiempirical and density functional methods. The previous two chapters were introductory, preparing for the major focus of the book, which is the theory and techniques of relativistic quantum chemistry. To find a chapter that, apart from the ECP section, is largely a prose overview of methods is odd, to say the least. The assumption of a high level of familiarity with quantum chemical methods and the resultant lack of detailed description does not fit with the intention to make a compilation of current techniques. Even the derivation of effective core potentials is more fully and lucidly developed in the original papers. It is quite incongruous that the author should go into great detail on topics that have little bearing on quantum chemistry, and skimp on the sections that have a direct bearing. It is also obvious that the author is mainly concerned with his own methods: some of the main developers of four-component methods are ignored entirely, and the description of methods other than ECP methods is very sketchy.

The final chapter, on double group theory, is the most well-written chapter. It presents a derivation of character tables for the extra irreducible representations in the double groups and the development of relativistic wave functions in terms of spatial and spin functions. It is amply illustrated and contains character tables for a number of groups, including those of the highest symmetry. It anything the explanations are a bit labored at times, and the chapter would have benefited from a brief introduction to group theory before launching into the construction of character tables, but the development is, in general, quite clear. As in the other chapters, there are some obscurities, omissions, and errors, but these are much fewer. One notable omission is the treatment of time-reversal symmetry and its connection to the double group.

After reading the book, the impression gained is not of a cohesive whole, but of a collection of separate sets of notes related to the theme but only loosely connected. Given the errors, the inconsistencies and the lack of clarity of many parts of the book, it is hard to judge the value of having these notes together in one volume. As a compilation of the author's own methods it has partially succeeded, and the group theory chapter contains useful information. As an introduction of relativistic quantum chemistry to the novice, it is far from adequate and liable to cause confusion. The need for such an introduction remains: this book may be timely, but timeliness alone is not enough.

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